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SUMMARY

Thin aluminum films have been considered for use as a reflective surface for solar collectors on orbiting solar dynamic power systems. A matter of concern is the durability of such reflective coatings against oxidative attack by highly reactive neutral atomic oxygen, which is the predominant chemical specie in low earth orbit. Research to date has been aimed at evaluating the protective merit of thin dielectric coatings over aluminum or other reflective metals. However, an uncoated aluminum reflector may self-protect by virtue of the oxide formed from its exposed surface, which constitutes a physical barrier to further oxidation. This possibility was investigated, and an attempt was made to characterize the effects of atomic oxygen on thin Al films using photomicrographs, scanning electron microscopy, spectrophotometry, Auger analysis, and mass measurements. Data collected in a parallel effort (to monitor specular reflectivity of various coated reflectors in an atomic oxygen environment) is discussed for its comparative value. The results of the investigation of uncoated aluminum supported the self-protection hypothesis, and importantly, it was found that long term specular reflectance for uncoated aluminum exceeded that of Al and Ag reflectors with dielectric coatings.

INTRODUCTION

A principal environmental hazard encountered in low earth orbit (LEO) is oxidation by ram impact of neutral atomic oxygen. Typical impacts carry a kinetic energy of approximately 4.2 eV at an altitude of 465 km, which is typical of space station altitudes (ref. 1). This kinetic energy could supply the energy of activation for thermodynamically feasible, oxygen radical-based reactions. To date, most research toward protection of solar reflector materials from oxidation has been focused on the use of thin film dielectrics such as SiO_2 , MgF_2 , and Al_2O_3 (refs. 2 and 3). These coated reflectors have an immensely increased resistance to atomic oxygen attack as compared to uncoated Ag reflectors. Losses in specular reflectance still occur, but at a much slower rate (refs. 2 and 3). If these losses could be eliminated completely, efficiency would be increased over the lifetime of a solar reflector.

Characteristics of the terrestrial oxidation of aluminum suggest that uncoated aluminum reflectors may self-protect, thus eliminating the need for an applied coating. In normal earth atmosphere, aluminum metal carries a surface layer of aluminum oxide a few tens of Angstroms thick, which is built

up from reaction with diatomic oxygen. This layer bonds well enough to the base metal that macroscopic signs of oxidation do not occur. If aluminum behaves analogously when reacting with monatomic oxygen, then one might expect a deeper Al_2O_3 layer to develop due to both the greater reactivity and greater diffusivity of atomic oxygen, after which the reactive oxygen specie is effectively blocked out.

The objective of this study was to investigate this self-protection hypothesis through observations of trends in specular reflectance (versus time in an atomic oxygen environment) to determine the viability of uncoated aluminum as a LEO solar reflector material.

Data collected in a parallel effort was used as a primary means of comparing the results obtained for uncoated aluminum reflectors with the performance of typical coated reflectors. In this parallel study, samples consisted of various candidate coated reflectors, and so provided an excellent basis for comparing the performance of uncoated Al reflectors with that of typical coated reflectors.

EXPERIMENTAL PROCEDURE

The samples consisted of analytical grade aluminum, magnetron sputtered at 500 W and 13.56 MHz onto optically flat, 2 cm squared, fused silica slides. The Al film thickness was 1800 Å, which is typical of film thicknesses under consideration for use in solar dynamic reflecting mirrors.

Verification of the growth of an adherent Al_2O_3 film was based largely on the presence of Al film defects (i.e., holes), in the samples used. From these, one may postulate an increasingly thin Al layer as one approaches the effective center of each defect (fig. 1). It is then reasonable to infer the existence of sites where the aluminum film becomes exceedingly thin - on the order of several atomic diameters - but is continuously intact. In these two types of structures, conversion of some given depth of aluminum to transparent aluminum oxide would either widen optical aperture widths or create optical apertures where none had existed. Therefore, the size and number of light-transmitting defects and the overall Al film transmittance would be expected to increase with exposure to atomic oxygen.

The size and number of light-transmitting defects was monitored by optical microscopy, with backlighting, at 22.5 to 500X magnification. Additional structural details were monitored using scanning electron microscopy (SEM) with magnification to 10 000X. Specular reflectance was measured over the wavelength region from 200 to 2 500 nm using a Perkin-Elmer Lambda-9 UV-VIS-NIR spectrophotometer operated with a 60 mm diameter integrating sphere. Average values for solar specular reflectance, obtained by convolution into the air-mass-zero (AMO) solar intensity spectrum (ref. 4), were calculated for quantitative comparison over time. Sample transmittance was obtained similarly, both spectrally and as an integrated solar value.

To simulate the LEO atomic oxygen environment, the samples were placed inside the reaction chamber of a Structure Probe Inc. Plasma-Prep II plasma asher. This device creates a plasma environment by passing a carrier gas (in this case ambient air) over the samples and exciting the gas with 100 W of

continuous wave rf power at 13.56 MHz. The operating pressure is about 50 μm . A direct relationship between exposure time in the asher and in LEO is difficult to determine, due to both the differences between space and the plasma environment in terms of species present, flux, energy, and electronic state, and to the current lack of space data for the materials concerned from which to construct correlations. However, use of the asher does allow gross determination of the relative likelihood of survivability of materials in LEO. The samples were removed from the asher at increasing intervals ranging from 20 to 112 hr for characterization and analysis.

As a final characterization technique, Auger depth profiles were performed on an aluminum reflector exposed to air plasma for 304 hr, and on one exposed only to atmosphere. Any differences in oxide depth and/or composition would provide further means of evaluating the self-protection hypothesis.

The construction of the coated reflector samples was somewhat different from that of the uncoated Al reflectors. For each coated reflector sample, a graphite-epoxy substrate was coated by evaporation techniques with either Al over Cr, or Ag over Cu, with the former of each pair acting as the reflective material, and the latter as a binder layer. As protective coatings, SiO_2 , MgF_2 , and MgF_2 over SiO_2 were then deposited to create six different types of composite reflectors. The SiO_2 coatings were deposited by evaporation, while the MgF_2 coatings were deposited by ion beam sputtering. Each layer was 1000 Å thick, with the exception of MgF_2 , which was 800 Å. While these samples were prepared differently from the uncoated Al reflectors, this does not prevent useful comparisons. The manner of asher exposure for these samples was identical to that of the uncoated Al samples, and SEM photographs and spectrophotometric data were similarly gathered.

RESULTS AND DISCUSSION

Optical Microscope Observations

The nominal diameter of the optical apertures in the 1800 Å Al film increased with asher exposure. At 23 hr, the largest aperture was 5 μm nominal diameter; at 192 hr, the largest was 23 μm (fig. 2).

The number of light-transmitting defects per unit area increased as ashing progressed. In the densest region at 23 hr, the aperture density was roughly $1.9/\text{mm}^2$, whereas at 192 hr the value reached $13.9/\text{mm}^2$ (fig. 3). This was calculated by manually counting the number of visible light-transmitting-defects in photomicrographs of known magnification. Defects which at first barely transmitted light continually became more transmitting. This can be seen qualitatively in figure 4.

These observations match the behavior expected as an oxide layer grows deeper where defects are present, as depicted in figure 1. Therefore, an enhanced degree of surface oxidation is indicated.

Spectrophotometric Measurements

The overall transmittance of the films increased with ashing time. This is apparent in the typical transmittance spectra presented in figure 5, and in

the integrated solar values, calculated from the transmittance spectra and plotted against asher exposure time (fig. 6). The scatter in this latter trend is due to an approach of the instrument precision limit, producing fluctuating transmittance values. These introduce a large relative random error, which was amplified in the use of a numerical integration technique.

Reflectance data gave additional support for the self-protection hypothesis. In the wavelength region from 200 to about 500 nm, a notable increase in sample reflectivity occurred as ashing progressed (fig. 7). This increase in reflectance might be expected when a thin film of Al_2O_3 is added to an Al surface.

Perhaps the most significant result was the long-term high specular reflectance of the samples. The performance of the uncoated Al films was exceptional, starting and remaining above 96 percent specular reflectance (solar weighted average, 200 to 2 500 nm), and in general, increasing with ashing time. This increase in solar reflectance is attributable to the noted increase in wavelength-specific reflectance in the shorter wavelength region (fig. 7). Of the coated reflectors, none were as reflective prior to ashing, and none had such long-term invulnerability to oxidative degradation of reflectivity. Each of the coated reflectors lost specular reflectivity as ashing progressed, with these losses becoming significant near 150 hr of ashing. Absolute specular reflectance versus plasma exposure time is presented in figure 8 for both uncoated Al and for the coated reflectors.

It should be noted that the optical flatness of the fused silica substrates was likely superior to that of the graphite-epoxy substrates. This might have contributed to the initial superior reflectance of the uncoated samples, and it could account for the difference in lifetime specular reflectance. A rougher surface may provide sites for coating defects to occur.

Auger Analysis

Analysis of both an ashed and an unashed sample by Auger Electron Spectroscopy showed no major differences in the thickness and composition of the respective oxide layers. In each case, the oxide layer thickness was about 100 Å. The ashed sample did, however, show a slightly higher O/Al ratio (1.2 versus 1.0). Since the ratio would be 1.5 if the surface consisted entirely of Al_2O_3 , it is reasonable to conclude that there was some elemental Al metal within the first 30 Å of the surfaces of both samples.

While the differences in Auger profiles between the ashed and unashed samples were not large, they could account for some of the observations discussed above. The increase in size and number of optical apertures clearly indicates an effect of the plasma. Since it was indicated from the Auger analysis above that there was some elemental Al within the first 30 Å of the surfaces of both samples, and, since there was a slightly higher O/Al ratio in the ashed sample, it is reasonable to assume that some of this surface elemental Al was converted to the oxide in the asher. Hence, it is also reasonable to suspect that areas of the Al film that were very thin initially (<30 Å, the optical near-apertures) consisted almost entirely of the metal-rich oxide. Conversion of this surface Al to translucent oxide would then be expected to cause the size and number of optical apertures to increase, as was observed.

Thus, the Auger analysis, coupled with the optical microscope observations, indicates that while oxygen plasma exposure does not cause an increase in surface oxide thickness, it still has a modest effect. The effect is seen as an increased degree of surface oxidation, occurring mainly in the first 30 Å or so of the surface.

Mass Measurements

Sample mass remained essentially constant throughout asher exposure. Calculations showed that an additional amount of Al_2O_3 (equivalent to about 50 "monolayers") would be necessary to measure a 10 µg increase in sample mass (the smallest measurable increment). Thus, the lack of a change in sample mass suggests that oxidation did not progress to this extent.

SEM Observations

No physical indications of any crumbling or flaking of surface layers could be seen. This reinforces the idea of a strongly-bonded oxide layer. Figure 9 presents examples of the highest magnification/resolution attained, wherein no spalling or flaking can be detected to a scale of about 10 Å.

Darkened patches on the surface film, visible under SEM, developed after 192 hr of ashing (fig. 10). The larger detail of figure 10 is the defect viewed in figure 4. Comparing figure 4(c) with figure 10, one can see that these darkened patches were not the new optical apertures observed in figure 3.

Under SEM, nodule formation was observed as a function of increasing ashing time (fig. 11). When silver is the reflective metal it is oxidized at coating fractures, where it must expand outward, since the molar volume of the oxide is 3.2 times greater than that of the metal. The expanding oxide plugs the defect so that the process is ultimately limited by rates of diffusion atomic oxygen through the oxide (ref. 5). It is unclear at this point what parallels may exist between this process and the development of the nodules observed in uncoated Al reflectors.

CONCLUDING COMMENTS

Aluminum apparently does self-protect in an oxygen plasma environment, evidently through good adherence of its native oxide. Due to the dielectric nature of Al_2O_3 , an increase in the effective oxide film depth, which resulted from an increased degree of surface oxidation (due, in this case, to oxygen plasma exposure), can enhance the specular reflectance.

REFERENCES

1. Banks, B.A., et al.: Protections of Solar Array Blankets from Attack by Low Earth Orbital Atomic Oxygen. Proceedings of the Eighteenth IEEE Photovoltaic Specialists Conference, IEEE, New York, 1985, pp. 381-386.

2. Morel, D.E., et al.: Solar Concentrator Materials Development. Advancing Toward Technology Breakout in Energy Conversion (21st IECEC), Vol. 3, American Chemical Society, 1986, pp. 2032-2038.
3. Gulino, D.A.; Egger, R.A.; and Banholzer, W.F.: Oxidation-Resistant Reflective Surfaces for Solar Dynamic Power Generation in Near Earth Orbit. NASA TM-88865, 1986.
4. Mirtich, M.J.; and Mark, H.: The Effect of Hypervelocity Projectile Material on the Ultimate Reflectance of Bombarded Polished Metals. NASA TMX-52981, 1971.
5. Gulino, D.A.: The Survivability of Large Space-Borne Reflectors Under Atomic Oxygen and Micrometeoroid Impact. NASA TM-88914, 1987.

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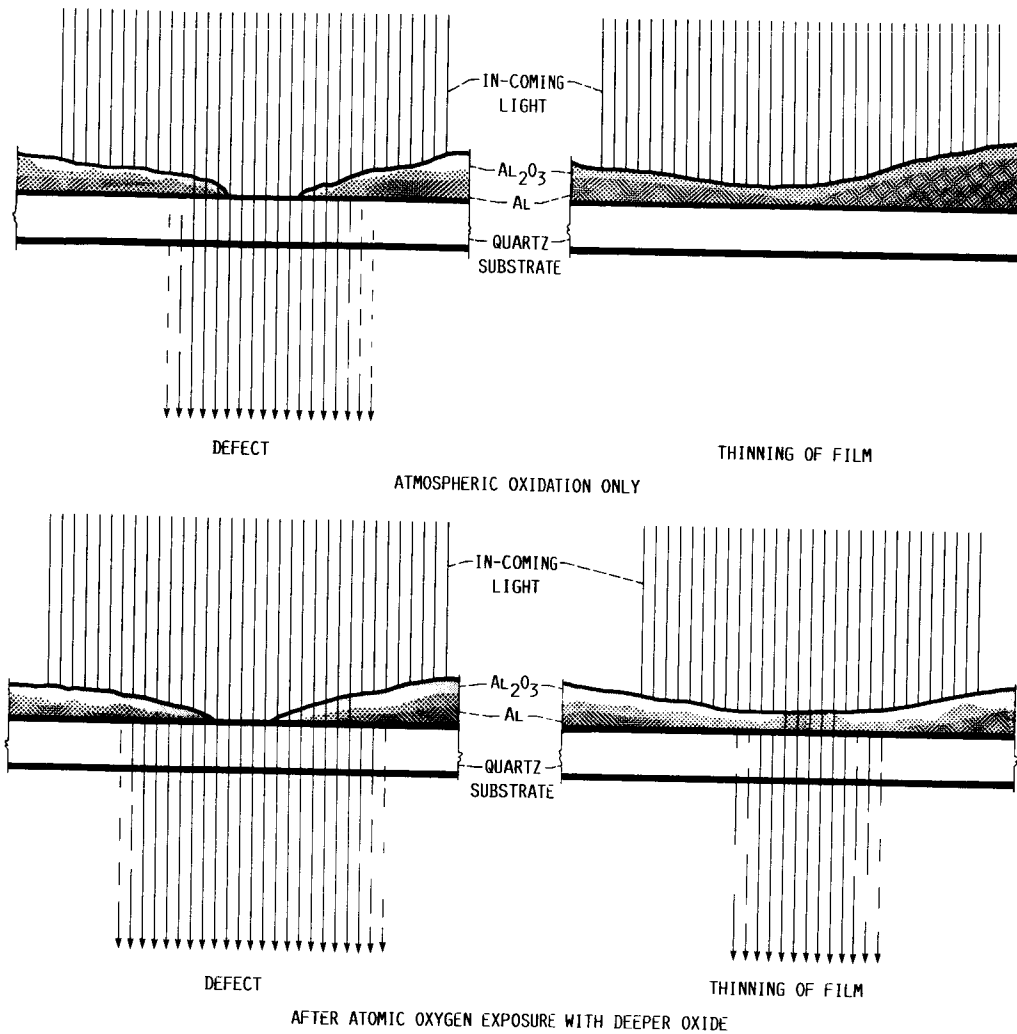
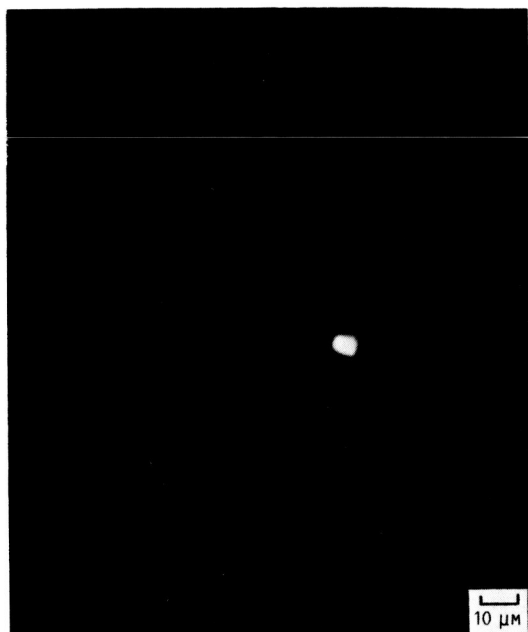
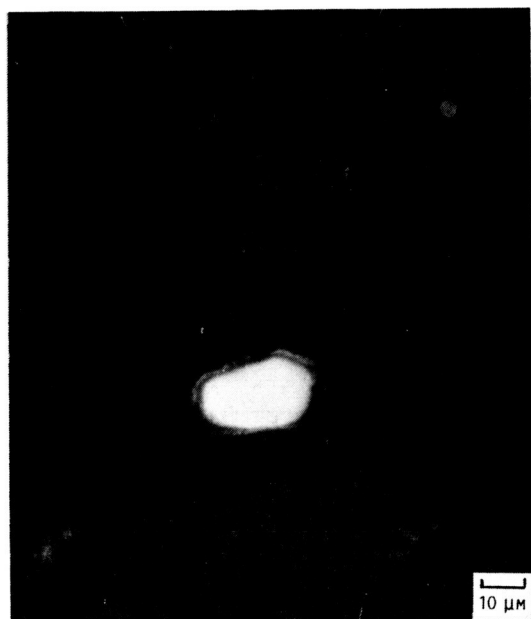


FIGURE 1. - TWO TYPES OF AL FILM DEFECTS BEFORE AND AFTER FURTHER CONVERSION TO AL₂O₃, ILLUSTRATING THE CHANGE IN THE OPTICAL APERTURE PRESENTED BY A DEFECT AND A THINNING OF THE FILM.

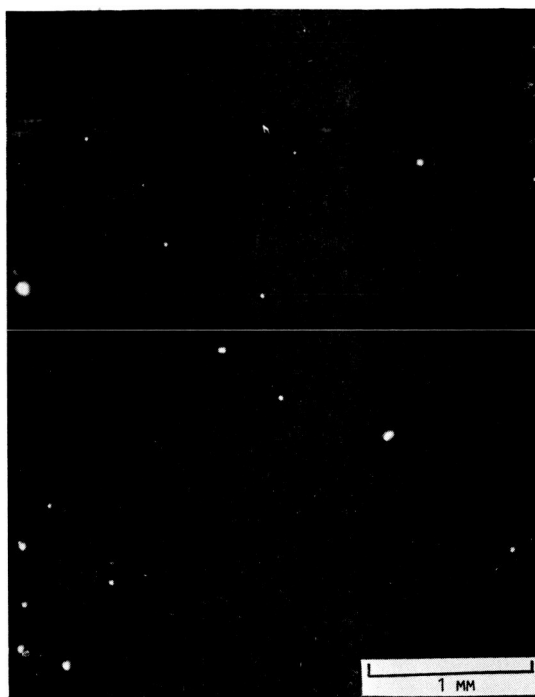


(A) AT 23 HR.



(B) AT 192 HR.

FIGURE 2. - SIZE OF THE LARGEST TWO OPTICAL APERTURES
IN AN AL FILM AS OXYGEN PLASMA EXPOSURE PROGRESSES.



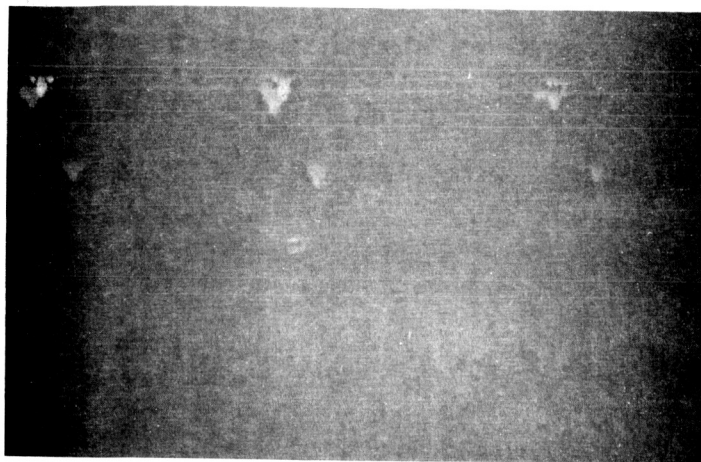
(A) DENSEST AREA AT 23 HR (DENSITY APPROXIMATELY
 $1.9/\text{mm}^2$).



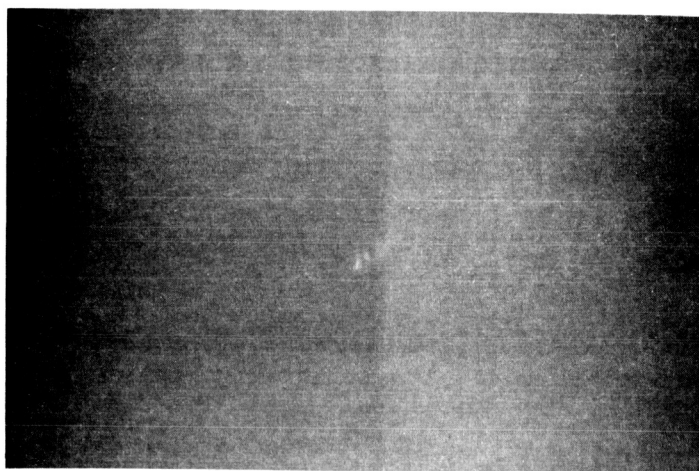
(B) DENSEST AREA AT 192 HR (DENSITY APPROXIMATELY
 $13.9/\text{mm}^2$).

FIGURE 3. - DENSITY OF LIGHT-TRANSMITTING-DEFECTS
IN AN AL FILM. REGION DEPICTED IN EACH PHOTOGRAPH
IS 0.137 CM.

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(A) AT 23 HR.



(B) AT 121 HR.



(C) AT 192 HR.

FIGURE 4. - INCREASE IN TRANSLUCENCY OF A DEFECT WHICH WAS INITIALLY ONLY SLIGHTLY TRANSLUCENT. SETTINGS WERE IDENTICAL FOR EACH PHOTOGRAPH.

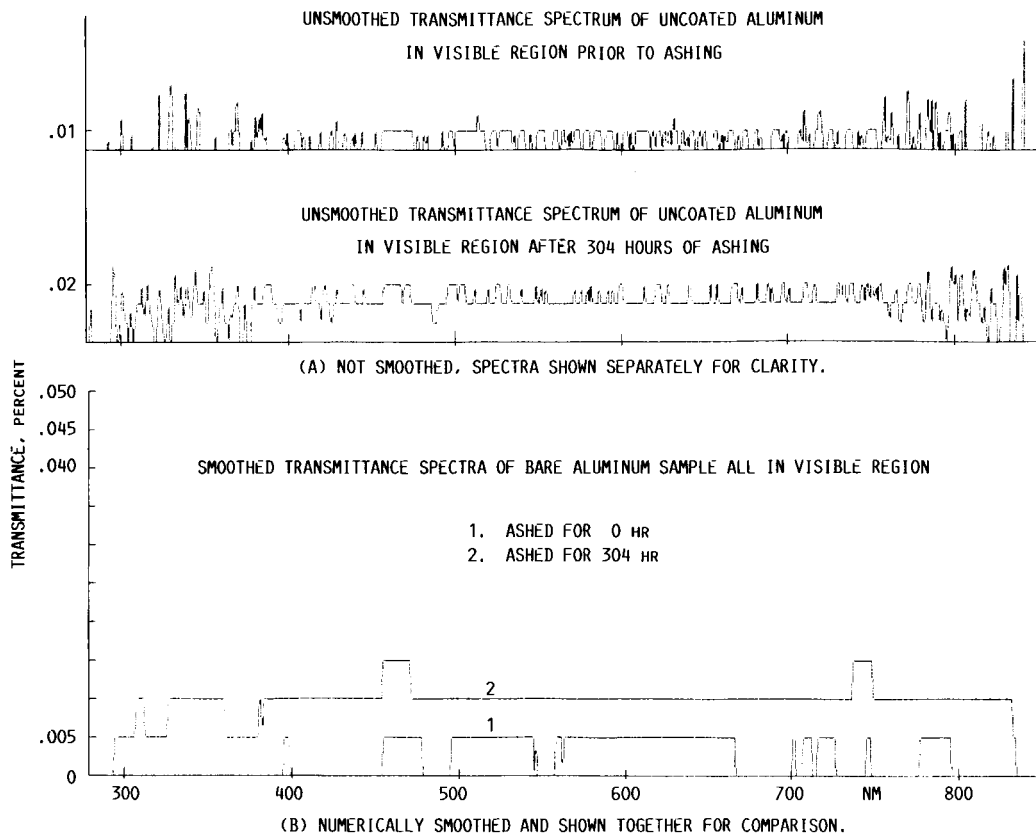


FIGURE 5. - TRANSMITTANCE SPECTRA OF A SAMPLE AT 23 AND 304 HR OF ASHING.

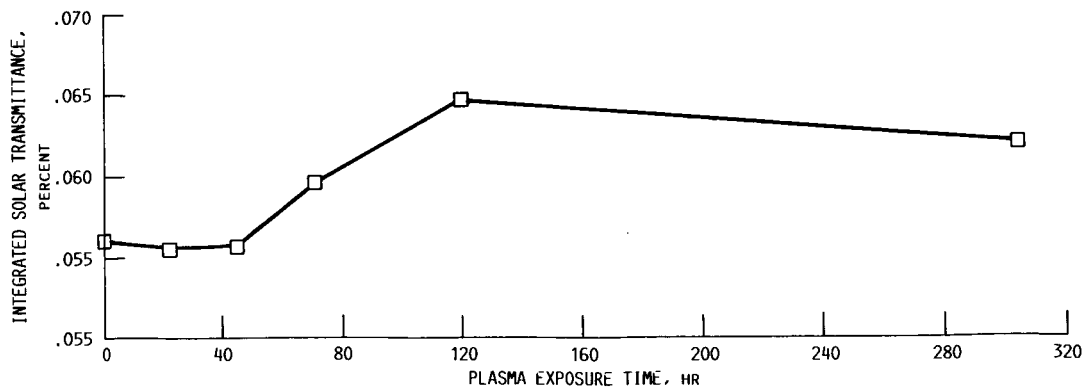


FIGURE 6. - INTEGRATED SOLAR TRANSMITTANCE PLOTTED AGAINST ASHING TIME.

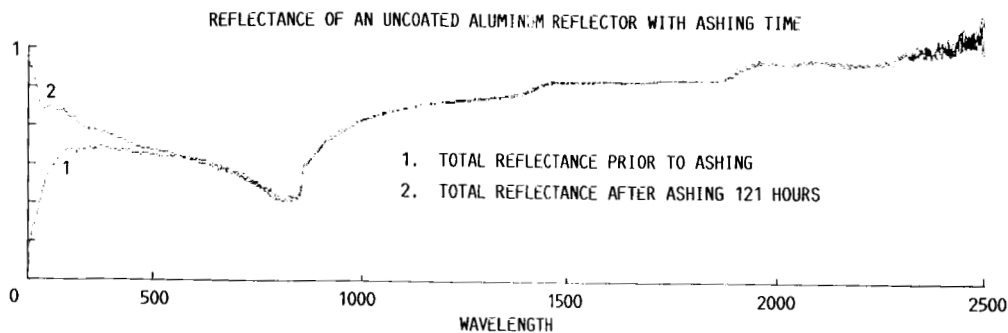


FIGURE 7. - TOTAL REFLECTANCE SPECTRA FOR ALUMINUM AT 0 AND 121 HOURS ASHING, INDICATING AN INCREASE IN REFLECTANCE COMMENSURATE WITH CONVERSION OF SURFACE AL TO Al_2O_3 .

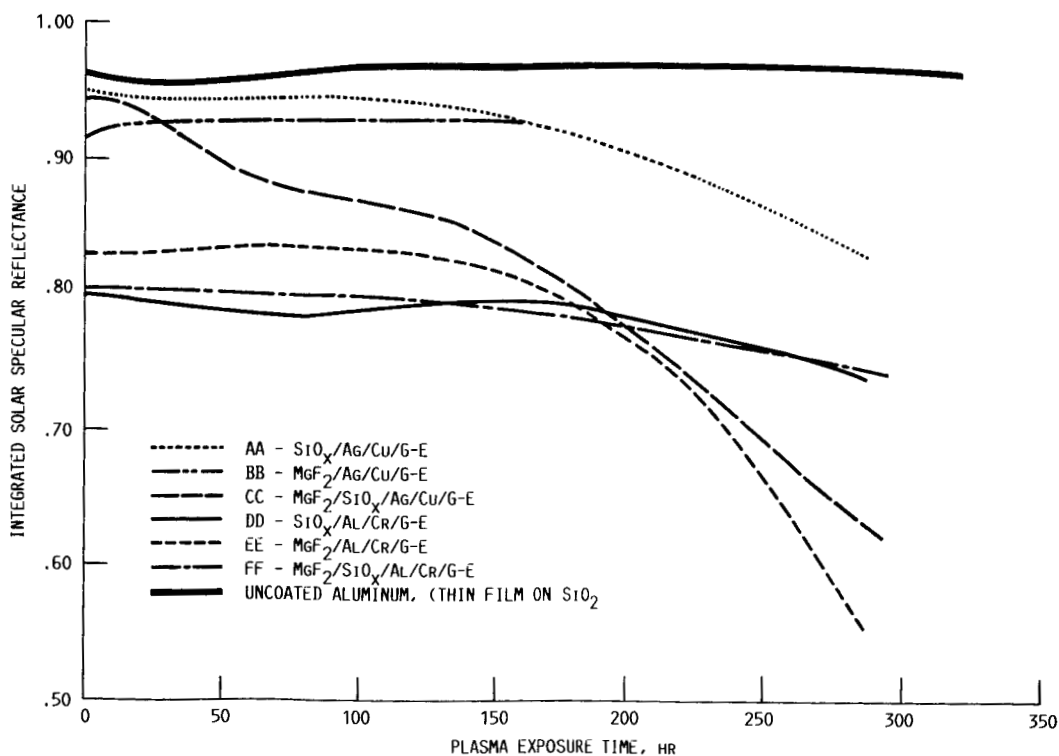
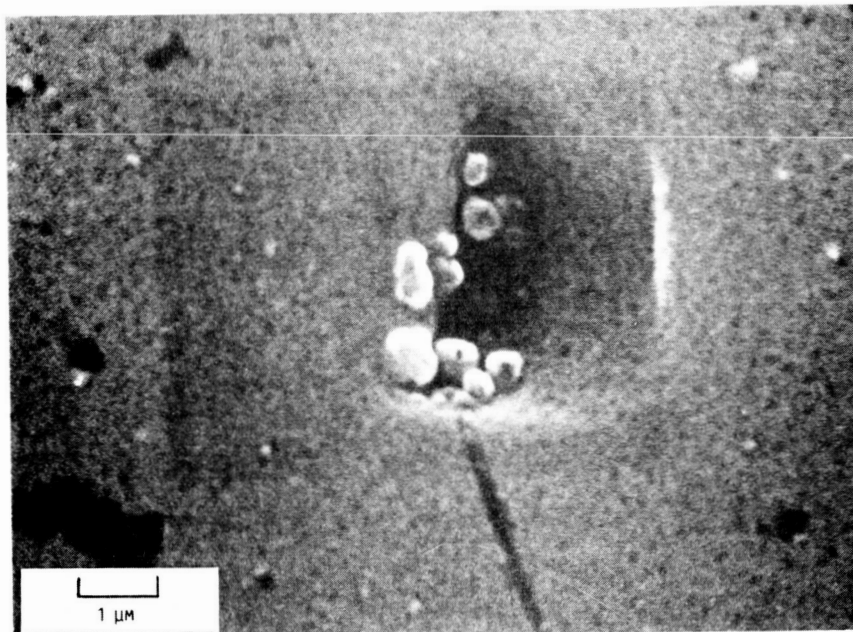
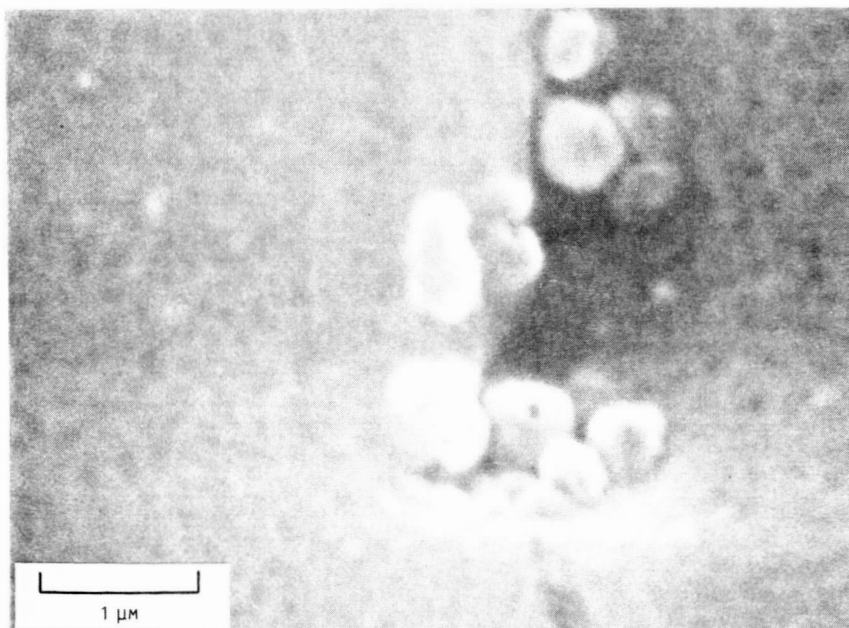


FIGURE 8. - PLOT OF SPECULAR REFLECTANCE FOR UNCOATED ALUMINUM AND VARIOUS COATED REFLECTORS, VERSUS TIME IN ASHER.

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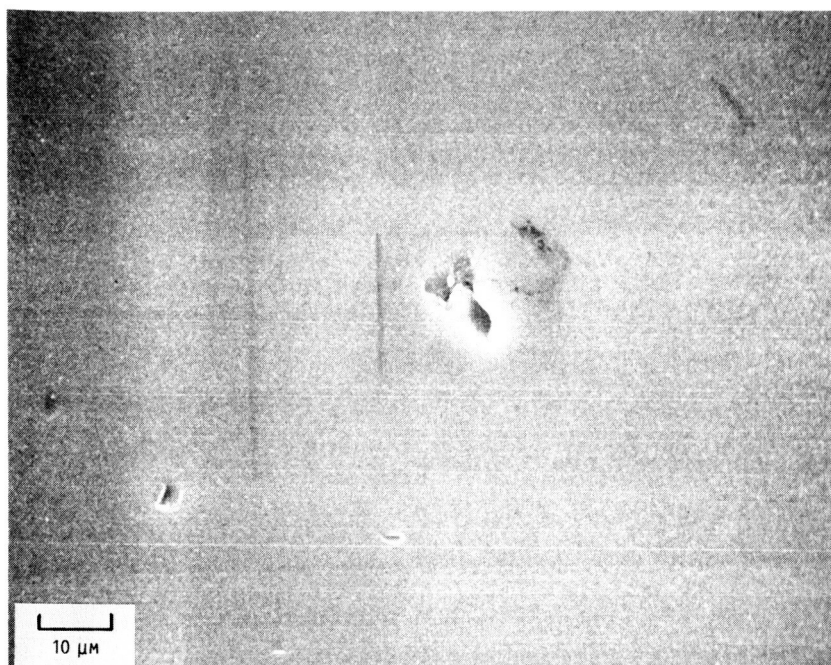
(A) LOW MAGNIFICATION.



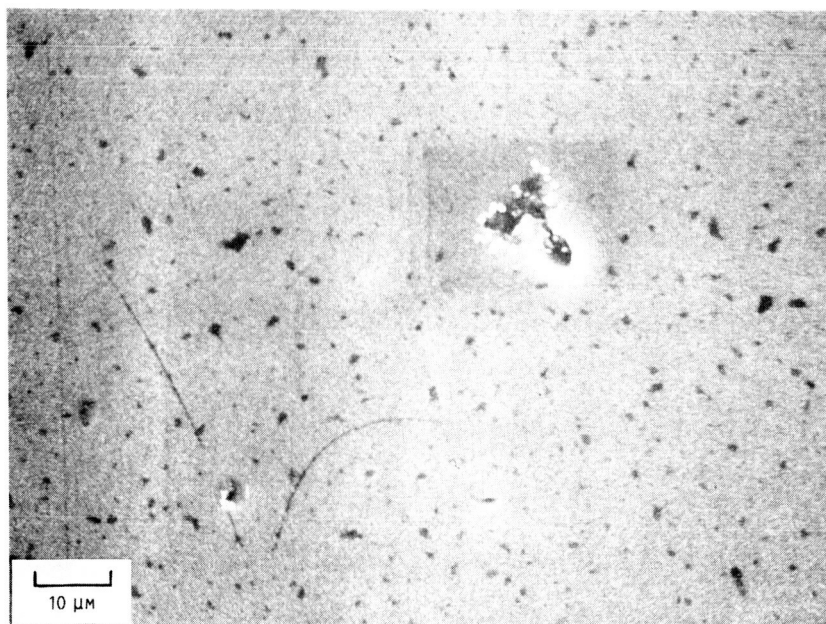
(B) HIGH MAGNIFICATION.

FIGURE 9. - EXAMPLES OF HIGHEST RESOLUTION ATTAINED WITH THE SEM. NO CLEAR SIGNS OF POOR OXIDE ADHERENCE. ASHED 192 HR.

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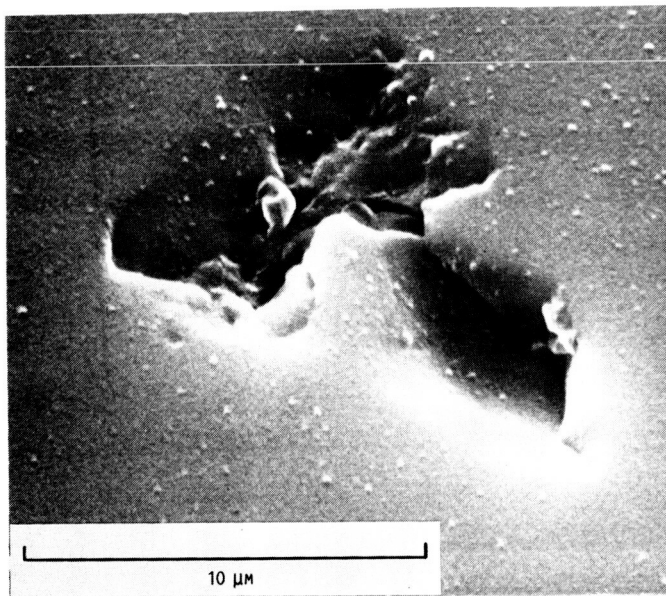
(A) ASHED 0 HR., NO DARK PATCHES.



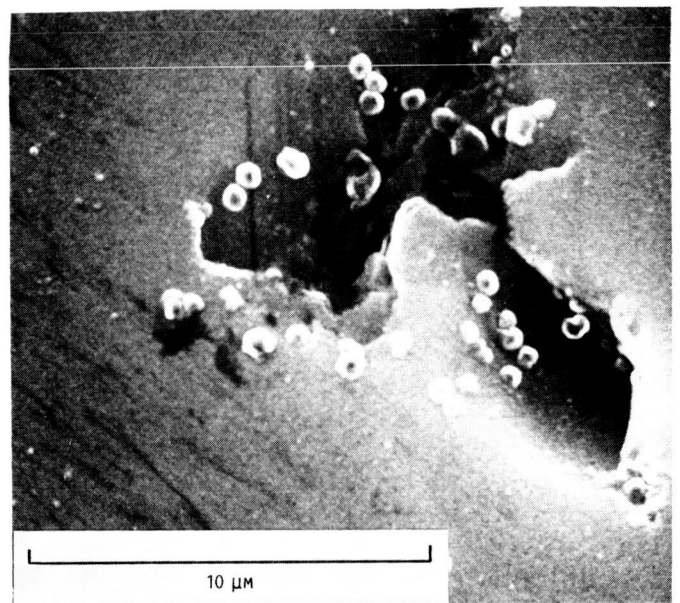
(B) ASHED 192 HR., NUMEROUS DARK SPOTS.

FIGURE 10. - DARKENED PATCHES (ON NONDEFECTED AL FILM) OBSERVED UNDER SEM.

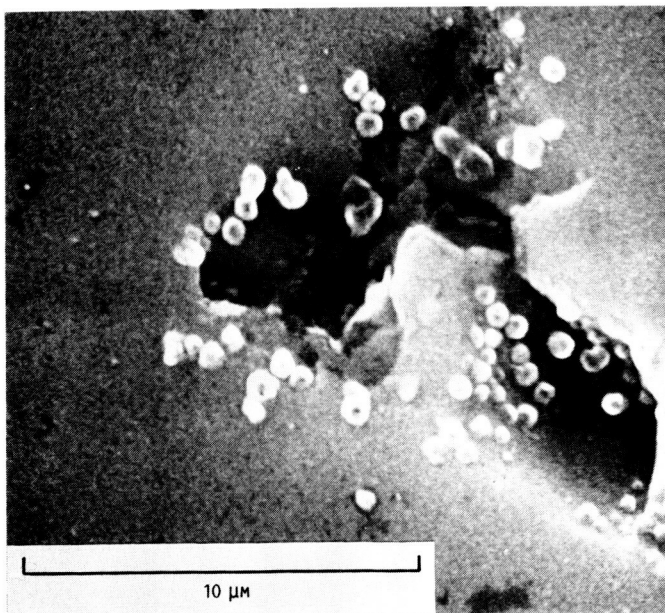
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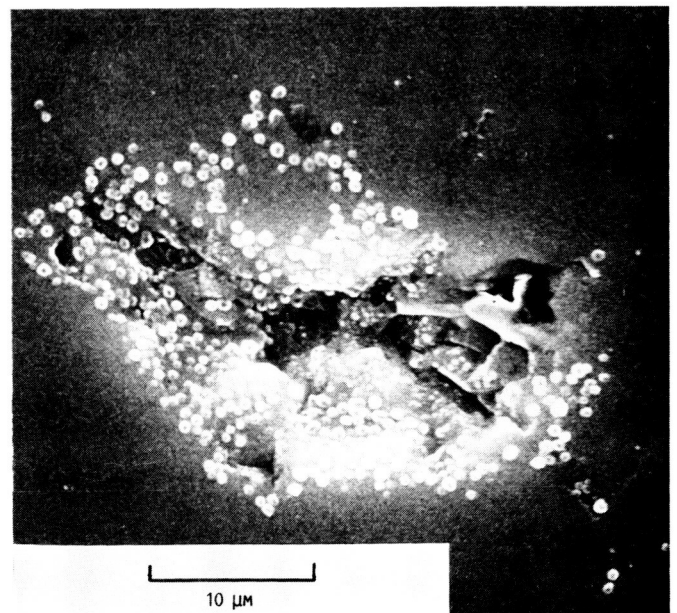
(A) ASHED 71 HR.



(B) ASHED 121 HR.



(C) ASHED 192 HR.



(D) ANOTHER DETAIL, ASHED 192 HR.

FIGURE 11. - EXAMPLES OF NODULE FORMULATION AS A FUNCTION OF ASHING TIME.

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